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# Low-temperature plasma ionization source for the online detection of indoor volatile organic compounds

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ABSTRACT

A simple-structure, low-power, and low-cost low temperature plasma (LTP) ionization source, coupled with mass spectrometry, for the online detection of indoor volatile organic compounds (VOCs) has been constructed in this work. Air, instead of noble gases, was employed as the discharging and carrier gas. And a custom-built AC high-voltage power supply with a total power consumption of 5 W, frequency of 2–4 kHz, and amplitude around 1–5 $kV_{p-p}$ was used. This LTP source is a soft ionization source. The initial performance of the ionization source has been evaluated by ionizing samples including alcohols, ketones, aldehydes and aromatics. These compounds cover most of the common air pollutants concerning people's health. It is well known that those plasmas generated by dielectric barrier discharge (DBD) produce significant amount of metastable species and electrons with mean energies greater than several electronvolt, but minimal fragmentation was observed in our work. Protonated ions are the dominant product for the VOCs detected after the ionization process. Further work has been conducted to confirm the detection feature of this source. The results are promising enough to ensure the novel LTP ionization source as an effective tool for the online detection of indoor VOCs.

## 1. Introduction

The determination and monitoring of volatile organic compounds (VOCs) has been gaining increasing attention in the past decades due to their serious detrimental effects on both the atmospheric environments and human health. Among those air pollutions caused by VOCs, indoor air contamination is of more importance to people's daily life. It is commonly generated by the emission of VOCs from man-made materials, especially those freshly synthesized ones. In recent years, the indoor air environment in homes has been deteriorating as a result of improved heat insulation and greater airtightness, which are the measures taken to save energy, but the problem of "sick house syndrome" has, as a result, become more widespread. Reports about discomfort and even poisoning caused by indoor VOC pollutions arose more frequently all around the world. VOC pollutions have also become a great threat particularly to those who work in a relatively closed environment, such as the manned spacecraft. Therefore, demands for the detection of indoor VOCs are growing rapidly.

Currently, the determination of indoor VOCs in air is officially performed by the standard analytical methods of gas chromatography (GC) coupled with various VOC detectors, mostly mass spectrometry (MS). MS is recognized as one of the best choices for molecular characterization of complex samples [1–3], due to its unparalleled ability to acquire detailed qualitative and quantitative information, as well as its exceptional sensitivity and specificity. The so-called GC–MS technique represents as an ideal tool when static or only slowly changing mixtures are to be analyzed and monitored, but online monitoring of mixtures with relatively fast changing concentrations remains problematic for it, because it is a time consuming method. Furthermore, pre-treatment including pre-concentration with cryogenic traps followed by desorption of target species is sometimes essential for GC–MS method. Finally, the use of GC leaves the method difficult to miniaturize, limiting its application in field and online detection [4].

Continuous efforts have been done to develop new methods for the analysis of complex mixtures of VOCs in ambient air. Proton-transfer reaction mass spectrometry (PTR-MS) is such a method that might complement the conventional GC technique. It was first proposed by Lindinger and his co-workers at the University of Innsbruck [5]. The proton transfer reaction (PTR) ionization is one of the chemical ionization (CI) methods, which enables fast online measurements of some important VOCs in air, including many

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oxygenated VOCs. It mainly produces protonated ions with less fragmentation than electron-impact ionization (EI) does. PTR-MS is well suited for the on-line study of VOCs. Outstanding as it represents, the PTR-MS method is limited in its applications in field measurements. A stable water vapor supply is essential during the testing process, and the demand for a semi-vacuous environment in the PTR source requires more power supply. Moreover, the relatively complicated structure leaves miniaturization a challenging work for this PTR-MS method. There is still a long way to go for this method.

At the beginning of this decade, the plasma physics community has actively been employed in the development of inexpensive low-temperature plasmas and plasma needles for industrial applications [6]. Na et al. first made use of dielectric barrier discharge (DBD) based plasma coupled with MS for the detection of explosives, as well as amino acids [7,8]. This emerged as an opening work. Since then, similar works of ambient ionization source based on plasma appeared rapidly. Quite recently, low-temperature plasma (LTP) has been introduced by Harper et al. as an ambient ionization source coupled with MS for the real-time analysis [9]. The LTP method makes use of DBD to generate cool plasma, which contains large amount of chemically active species including high-energy electrons, metastable neutrals, and radical ions [9]. The plume of the LTP source allows for the analysis of different types of molecules, regardless of the actual existing form of the sample, and without any additional sample pretreatments [10–14]. In general, LTP sources have the advantages of low power consumption, low operating temperature, and being environmentally friendly. But the necessary employment of rare gases for discharging brings trouble to all current LTP ionization sources when faced with field detection. Air, if possible, would be preferred to maintaining the LTP.

In our work, a novel design of a LTP ionization source, coupled with MS, for the simultaneous online detection of indoor VOCs has been introduced. Molecular ions are usually the dominant ionized species for common indoor VOCs. This allows simultaneous detection without pre-separation. Different kinds of common indoor VOCs were detected to demonstrate the source's performance. Air, instead of noble gases, was employed for discharging and carrying. No additional rare gases were needed. The structure of the source has well been simplified with low weight, low power consumption, and small in volume. Conditions have been optimized for this new LTP source.

## 2. Experimental

### 2.1. Chemicals and reagents

All reagents and chemicals were used as received without further purification. Chemicals including 99.5% pure methanol, 99.7% pure ethanol, 99.7% pure isopropanol, 99.5% pure acetone, 99.5% pure benzene, and 30% pure formaldehyde water solution were purchased from Beijing Chemical Plant. Butanone was also purchased from Beijing Chemical Plant, and its boiling range is 78.5–80.5 °C.

### 2.2. Design of the LTP source

The configuration of the designed ionization source in this research is shown in Fig. 1. The LTP source includes a quarts fork tube with inner and outer diameters of 2.0 mm and 4.00 mm, respectively. A copper wire acting as an internal electrode was centered inside one branch of the quarts tube. A thin tin foil paper surrounding the outside of the quarts tube was used as the outer electrode. A custom-built AC high-voltage power supply (1–5 $kV_{pp}$, with a frequency of 2–4 kHz) provided adequate voltage to the internal and external electrodes for the generation of dielectric barrier discharge. The total power consumption of this LTP source is 5 W. The distance between the LTP source and the ion entrance capillary of the LTQ instrument is 1 cm. Local air was employed as discharging medium for the formation of low temperature plasma in one branch of the fork tube (70 mL/min). A second current of air carrying sample molecules was injected in another branch of the fork tube (600 mL/min). And sample molecules went into the second air current all by their natural evaporation under room temperature.

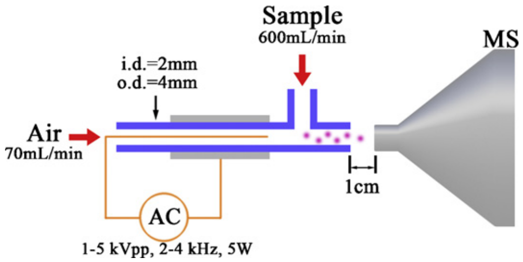

**Fig. 1.** Schematic side view diagram of the LTP device. Sample molecules were carried by air into the tube.

### 2.3. Instrumentation and LTP operation

All experiments were performed on a commercial Thermo Fisher LTQ (San Jose, CA) linear ion-trap mass spectrometer equipped with our self-made LTP ionization source. Xcalibur software 1.4 SR 1 was used for data acquisition. Positive-ion detection mode was used for all the research in this work. The instrument was set to collect spectra in automatic gain mode for an ion trap injection time of 200 ms at 2 microscans per spectrum. Power was supplied by a home-made ozone generator. The LTP device was operated at a constant voltage. Samples carried by air were injected into one branch of the fork tube to mix with the plasma generated from another branch of the tube for ionization. The outcome of the mixture was then induced to MS detector for further measurement.

## 3. Results and discussion

### 3.1. Characteristics of the LTP source

To better meet the requirements for field applications, the source was well programmed. As illustrated in Fig. 1, the structure was designed as simple as possible. The chief discharge type in this work is believed to be low-current atmospheric pressure dielectric barrier discharge, which takes place between the inner and outer electrodes as air passes through the tube. Such kind of discharges generates non-equilibrium, low-temperature plasmas that generate chemically active species such as meta-stable neutrals, high-energy electrons, and radical ions. It is these primary particles that then ionized sample molecules through complicated processes of collisions and reactions.

### 3.2. Performance of the LTP source

To demonstrate its ability of ionizing common VOC molecules, different kinds of VOCs including alcohols, ketones, aldehydes, esters and aromatics were investigated. These compounds were chosen because they are the most common air pollutants. Fig. 2 illustrates the performance of the LTP device for ionizing ethanol, acetone, formaldehyde, ethyl acetate and benzene, respectively.

For ethanol and acetone, $[2M+1]^+$ is the dominant ion. Actually, dimerization is commonly observed in many of the plasma

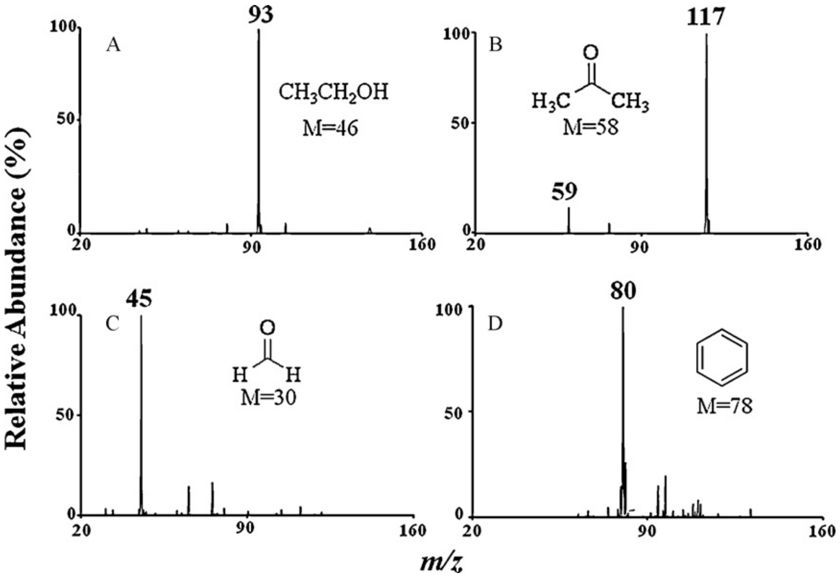

**Fig. 2.** Mass spectra of (A) ethanol, (B) acetone, (C) formaldehyde, and (D) benzene, respectively.

mass spectra. This phenomenon is common to both alcohols and ketones, especially for alcohols. Further experiments have been conducted to verify the formation of $[2M + 1]^+$ when ionizing alcohols and ketones. For alcohols, not only ethanol, but also methanol and propanol tend to dimerize when ionized. Fig. 3 shows the mass spectra of methanol and propanol acquired in positive mode. They are similar to the mass spectrum of ethanol. Although there is a great tendency of dimerizing, monomer ions do exist. To enhance the monomer peak on a mass spectrum, the concentration of the alcohol should be controlled to be very low. There should be a balance between the monomer and the dimer.

Similar phenomena concerning protonated water clusters have previously been reported. In some plasma based ionization source, protonated water clusters ($(H_2O)_nH^+$) with $n = 2–4$ in majority dominated the background [15,16]. Water cluster with $n = 2$ usually had the highest concentration. Similar water cluster distributions have been modeled by a process starting with a Boltzmann-like distribution with $n = 4–10$, followed by fast decomposition of larger water clusters into smaller ones of the $n = 2–3$ clusters at the ionization interface [17]. The almost distinct lack of hydronium ion ($H_3O^+$) is a result of its lowest proton affinity of all the protonated water cluster ions, that is, a single water molecule is not able to “solvate” the proton efficiently. While ion beam experiments have been conducted to prove that proton affinities of $(H_2O)_nH^+$ increase with $n$, the dynamic stabilities of water clusters go the opposite way, and decrease with $n$. The balance of thermodynamic stabilization and dynamic decomposition gives water cluster with $n = 2$ as the densest species.

Alcohol molecules have many similar properties with water molecule, for both the two kinds of molecules have hydroxyls. The existing oxygen atom with strong electronegativity in hydroxyl makes such kind of molecules easily attracted by positively charged proton. The formation of dimer alcohol ions could be well explained similarly like water. Taking into account of the fact that alcohols have far lower polarity compared to water, it would be quite difficult for alcohols to form larger clusters than dimer cluster. That is why no larger clusters could be found according to the spectra obtained. The formation of these dimer clusters well confirmed that this LTP source is a soft ionization source.

Similar to alcohols, ketones also tend to dimerize when ionized. To further look into the ionization properties of ketones, butanone was investigated as well (data not shown). Both acetone and butanone dimerized during the ionization process, but obviously not so easy as alcohols. This may be caused by their even lower polarities compared to alcohols.

According to the acquired spectrum of formaldehyde in Fig. 2, neither $[M + 1]^+$ nor $[2M + 1]^+$ could be found to be present. The peak at $m/z = 45$ is believed to be generated by $[CO_2H]^+$. As a result of its strong reducibility, formaldehyde is oxidized quickly in the plasma atmosphere. Further experiments have been conducted to get to know if $CO_2$ would interfere with the measurement of formaldehyde. Diluted sulfuric acid was dropped into powdered calcium carbonate to produce $CO_2$. The detection of such $CO_2$ showed no signal at $m/z = 45$. Actually, $CO_2$ has a quite low proton affinity, it is difficult for it to get ionized by proton. We believe that the formation of $[CO_2H]^+$ should be caused by the formaldehyde's

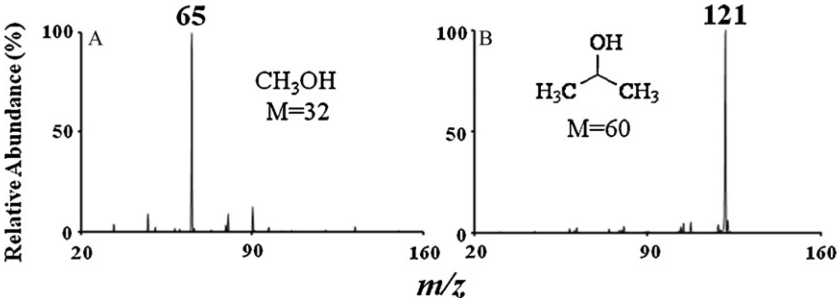

**Fig. 3.** Mass spectra of (A) methanol and (B) isopropanol.

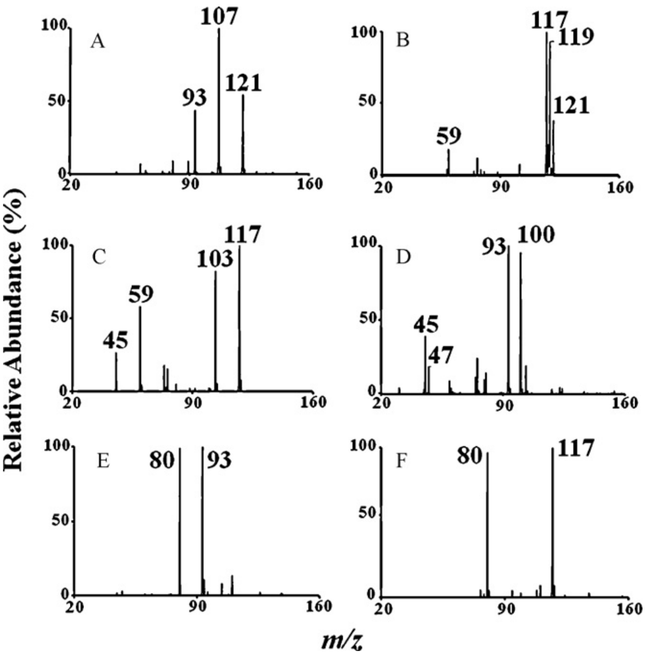

**Fig. 4.** Mass spectra of (A) ethanol and isopropanol, (B) isopropanol and acetone, (C) acetone and formaldehyde, (D) formaldehyde and ethanol, (E) ethanol and benzene, and (F) acetone and benzene.

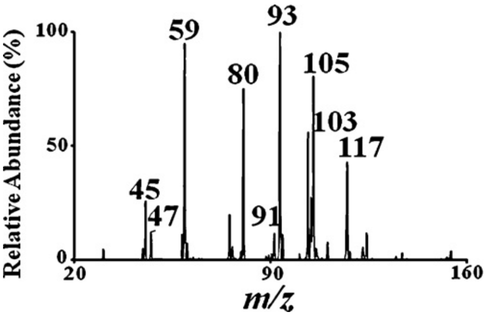

**Fig. 5.** Mass spectrum obtained from the multicomponent detection experiment.

protonation before it is completely oxidized into $CO_2$. Besides formaldehyde, no other aldehyde would be oxidized during the ionization process, and their ionization behaviors resemble ketones. Experiments have been carried out to verify this.

For aromatic compounds, $[M+2]^+$ ions are the predominant ions (Fig. 2D). This is due to the reduction of those aromatic compounds by the plasma. Similar results have previously been reported by others, with the ionization mechanism well discussed [18].

Quantitative detections have also been conducted to better evaluate the source's detecting ability of VOCs. The LODs of acetone, isopropanol, and benzene were studied as representive compounds of ketone, alcohol and aromatic compounds. The detection limits of these three compounds are 80 ppb, 200 ppb, and 3 ppm, respectively.

To further demonstrate the LTP source's ability of detecting multicomponent samples, different binary combination of the VOCs mentioned above were detected using the LTP device. Results were shown in Fig. 4. Fig. 4A illustrates the simultaneous detection of ethanol and isopropanol. The peaks at $m/z=93$ and $m/z=121$ are identified as protonated dimer clusters of ethanol and isopropanol, respectively. In addition, a peak at $m/z=107$ was observed, which was even higher than the two peaks at $m/z=93$ and $m/z=121$. The height of this peak represented the highest concentration among all the ions detected. This peak was assigned to the interdimerization of ethanol and isopropanol molecules. To be specific, it was the dimerization of one ethanol molecule and one isopropanol molecule that formed the certain protonated cluster ($[CH_3OH{\cdot}C_3H_7OH{\cdot}H]^+$). The reason why this interdimer was the most abundant was the randomly combination of the molecules with each other. The possibility of the collision of different compound molecules is twice as much as that concerning the same compound molecules. If inter compound dimerization is thermodynamically as easy as the dimerization of the same compound, and the difference between the initial concentrations of the neutral compounds is not that great, then there would surely be more interdimers. This is just the case of the ethanol and isopropanol mixture. For other mixtures, the relative signal intensities of different ionized species may not resemble that of the ethanol and isopropanol mixture, due to the various thermodynamic stabilities of different ionized species, and the diverse concentrations of mixture components. Similar to alcohols, ketones also tend to form inter compound dimers.

For mixtures of different kinds of compounds, such as the mixture of an alcohol and a ketone (Fig. 4B), the mixture of a ketone and an aldehyde (Fig. 4C), or the mixture of an alcohol and an aldehyde (Fig. 4D), inter compound dimers appeared as well. The common oxygen atoms of these compounds enable them be attracted by protons simultaneously. Those peaks representing $[M{\cdot}M'{\cdot}H]^+$ clusters are of great importance because they could further conform the peaks representing $[2M{\cdot}H]^+$ clusters, especially when the $[M+M'+1]$ signals are even stronger than $[2M+1]$ signals.

Compounds with no oxygen atom presented no dimerization with other compounds, nor did they dimerize with themselves (Fig. 2D). Detecting result of benzene and ethanol mixture is shown in Fig. 4E. This mass spectrum is a simple addition of pure benzene's spectrum with pure ethanol's spectrum. Similar is the mass spectrum of benzene and acetone mixture (Fig. 4F).

### 3.3. Simulative detection

At last, a simulative detection of an artificially prepared multicomponent sample was carried out to confirm the performance of the LTP device. This sample contains four different components including ethanol, acetone, benzene, and formaldehyde.

The detecting result is shown in Fig. 5. The peak at $m/z=45$ represents $[CO_2H]^+$, which indicates the existence of formaldehyde in the sample. The peaks at $m/z=93$ and 117 represent $[(C_2H_5OH)_2H]^+$ and $[(CH_3COCH_3)_2H]^+$, respectively, which indicate the existence of ethanol and acetone in the sample. The peak at $m/z=80$ represents $[C_6H_8]^+$, which indicates the existence of benzene in the sample. The peaks at $m/z=59$ and $m/z=47$ represent $[(CH_3COCH_3)H]^+$ and $[(C_2H_5OH)H]^+$, respectively, which confirm the existence of acetone and ethanol.

The peak at $m/z=105$ stands for the inter dimer of ethanol and acetone, which further demonstrates the existence of ethanol and acetone at the same time. Similarly, the peak at $m/z=103$ demonstrates the presence of acetone and formaldehyde at the same time, and the peak at $m/z=91$ demonstrates the presence of ethanol and formaldehyde at the same time.

In conclusion, according to the mass spectrum acquired, this sample measured consisted of formaldehyde, ethanol, acetone and benzene. These compounds indeed were the actual constituents of the sample.

## 4. Conclusions

An ambient LTP ionization source based on dielectric barrier discharge has been developed for the simultaneous detection of indoor VOCs. Results obtained well confirmed it to be an effective soft ionization source for different kinds of VOCs. Protonated dimer clusters prove to play an important role in the ionization process, and are usually the main species. This developed LTP-MS device holds several advantages over GC–MS and PTR-MS including real-time detection, simple structure, low cost, easy to miniaturize and feasible for field detection. Regardless of these advantages, efforts are still needed for quantitative detection. And the detection limits need to be further lowered. Moreover, the ozone generated by discharging should be removed, in case it may pollute the environment. Experiments to look into these problems are currently underway so as to better improve the source's performance. If successful, this would be a promising for the field online detection of indoor VOCs.

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